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GROWTH OF SILICON NANOSTRUCTURES BY THERMAL EVAPORATION USING NICKEL CATALYST

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ABSTRACT

One dimensional silicon nanostructures were synthesized by thermal evaporation technique using nickel catalyst. The silicon powder that served as a starting source material was evaporated at 1050°C in nitrogen gas flow. Nickel-coated Si(111) substrate was used to collect the silicon nanostructure products that positioned at 3 to 12 cm from the source material. By controlling the growth temperature, duration and substrate location the silicon nanostructures have been succesfully produced. The FESEM equipped with EDX spectrometer was used to investigated morphology and elemental composition and TEM for investigation of size and shape of silicon nanostructures. Needle-like silicon nanowhiskers with a spherical tip is the most obtained nanostructure products. The EDX measurements confirmed the silicon structure of the nanowhiskers and the existence of a nickel dot on the tip. Therefore, the vapour-liquid-solid (VLS) mechanism was proposed for growth process of the silicon nanowhiskers.

INTRODUCTION

One-dimensional silicon nanostructures have attracted much attention in recent years for their valuable electrical and optical properties, as well as their potential applications in mesoscopic research and nanodevices [1]. Silicon nanowires have recently become of interest for potential applications in various technologies such as optics, electronics, and chemical sensors. Silicon nanowires can offer the possibility of integration with conventional Si integrated circuit technology [2].

Common method of silicon nanowires growth is vapour–liquid–solid (VLS) mechanism, in which a catalyst metal droplet acts as a site for vapour-phase adsorption of Si atoms [3]. Nanowires obtained by such a crystal growth mechanism are catalyzed by a metal eutectic nanodroplet. Metallic nanoparticles play a key-role in the VLS process. Due to its physical and chemical properties, a gold catalyst is frequently used. Most of these methods metal catalyst such as nickel (Ni) or copper (Cu) can be used to control the critical nucleation. Zhou and co-workers [4] demonstrated that homogenous nanowires diameter can be controlled by the size of the catalyst droplet.

The field of nanoscale research covers a wide range of materials in the fields of nanosize scale. There are many types of nanoscale or other name nanostructure material like nanoparticles, carbon nanotubes, nanowires, and nanoporous materials.

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Nanoparticles are zero dimensional nanostructures, which includes single crystal, polycrystalline, and amorphous materials with all possible morphologies, such as spheres, cubes, and platelets. Nanotubes and nanowires are some of one dimensional nanostucture materials, as example is carbon nanotube. A carbon nanotube is like structure that results from special arrangement of carbon atoms. Carbon nanotubes are nanometer wide tubular arrangements of hybridized carbon atoms. Nanowires were expected to play to key-role as well as for potential nanotechnology applications. Semiconductor nanowires have been studied intensively over the past year due to their potential applications for nanoscale device fabrication. Typically, these nanostructures are cylindrical single crystals with a diameter of 10 nm to 100 nm and a length of several microns. The ability to predictably control their properties makes nanowires particularly promising to be used as a building block for the next generation of nanoscale devices.

Several nanowire growth mechanisms have been developed, such as template-assisted synthesis, laser ablation, chemical vapour deposition (CVD), electrochemical deposition, or vapour-liquid-solid (VLS) approach. By using these different techniques, a large variety of semiconducting nanowires have been observed. Most of the recent successful semiconducting nanowire growth is based on the VLS technique. VLS growth is commonly referred to as either impurity or catalyst, which purposely introduced to direct and confine the crystal growth on to a specific orientation and within a confined area. A catalyst forms a liquid droplet by itself or by alloying with grown material during the growth, which acts as a trap of growth species. Enriched growth species in the catalyst droplets subsequently precipitates at the grown surface resulting in the one dimensional growth [5]. Silicon whisker was first shows by Wagner and Ellis in 1964 [6] for the growth of silicon whiskers with diameters from one hundred nanometers to hundreds of microns. But due to the recent need for systematic nanostructure synthesis and the progress in the formation technique of metal nanosize particles, there is a renewed interest in the VLS technique. Metallic nanoparticles play a key-role in the VLS process. Nanowires obtained by such a crystal growth mechanism are catalyzed by a metal eutectic nanodroplet.

The use of nickel as a catalyst for the silicon nanowire growth seems promising. Thermodynamically, nickel is compatible with the VLS assisted silicon nanowire growth. Phase diagram is also helpful for estimating the optimal composition and temperature for nanowire growth. The phase diagram of the Ni-Si alloy shows eutectic reactions at 964 °C, 966 °C, 1143 °C, and 1215 °C [7]. Nanowires will form at eutectic temperature. A thermal evaporation method has been used in this study. This method widely used due to its advantages in obtained silicon nanowires, which rich in different morphology in different deposition regions under the same processing. Silicon nanowires can be synthesized via thermal evaporation method without catalyst. However, silicon nanowires products difficult to growth in preferred orientation. To produce high quality silicon nanowires, some researchers use gold catalyst. Since Au catalyst consider expensive metal, therefore in this work nickel was used as metal catalyst for cheaper cost production.

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EXPERIMENTAL METHOD

Synthesis method of one-dimensional silicon nanostructures is similar to our previous work [8]. However, in the current work, nickel was used as a catalyst without activated carbon source to grow one dimensional silicon nanostructures. The source material was prepared by grinding silicon powder (Aldrich, purity: 99.0%) by agate mortar to form homogeneous powder. The p-type Si(111) wafer (1 cm x 2 cm in size) was subjected to standard RCA cleaning. Pre-cleaned substrate was then spin-coated by a very thin layer of nickel. The source material was loaded in a quartz boat and inserted in the centre of the horizontal alumina tube furnace. The nickel-coated Si substrates were placed downstream horizontally on a quartz boat adjacent to the source material with a distance of 3, 6, 9 cm, respectively; and a vertically-positioned substrate was placed 12 cm from the source material. The quartz tube was pumped-down by a mechanical vacuum pump for several minutes before purged with high-purity nitrogen gas to eliminate oxygen in the system. Then, the chamber was heated up to a pre-set temperature (1050 ^{o}C) at a designed heating rate of 20 ^{o}C min^{-1} under nitrogen flow. Upon reaching the desired temperature, the whole system was maintained at certain soaking time (1 hour) before slowly cooled down to room temperature. The growth product was then examined by a field emission scanning electron microscopy (FESEM) equipped with energy dispersive x-ray (EDX) spectrometer (Zeiss SUPRA 35VP) and transmission electron microscopy (TEM) (Philips CM12).

RESULTS AND DISCUSSION

In VLS mechanism, diameter of liquid metal catalyst droplets delivered on the silicon substrate is one of important parameter. Therefore, it is important to control the size of catalyst droplets [5]. In this work, nickel nitrate ($Ni(NO_3)_2.6H_2O$) was used as the source for nickel to initiate the silicon nanostructure nucleation. In order to avoid oxidation, $Ni(NO_3)_2.6H_2O$ solution was dissolved into ethanol (C_2H_6O). Spin coating technique was used to deposit a very thin layer of nickel on silicon substrate. Figure 1 shows the distribution of nickel cluster on silicon substrate. The clusters are normally consists of small size particles that can be used as a seed to grow nanowire or others one dimensional nanostructures.

Effect of substrate location and distance from the source material on the preparation of nanostructures was studied by positioned horizontally at 3, 6 and 9 cm; and one vertically at 12 cm from the source material. The growth temperature of 1050 °C for 1 hour was applied to the current work. The needle-like nanostructures with diameter in range 25 nm to 80 nm and length is around 200 nm to 1100 nm was found in the substrate located 3 cm as shown in Figure 2 (a). These irragular shape of nanostructures are grown outward from the silicon substrate. The other samples are also showing the similar needle-like structures (Figure 2 (b)-(d)). However, sample at 6 cm has bigger needle size (Figure 2 (b)), meanwhile, samples positioned at 9 cm or farther produce

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Solid State Science and Technology, Vol. 16, No 1 (2008) 100-106
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finer and better nanoneedle structures (Figure 2 (c), (d)). Therefore, it was suggested that location between 9 to 12 cm is optimum distance of substrate from source to grow a better structure.

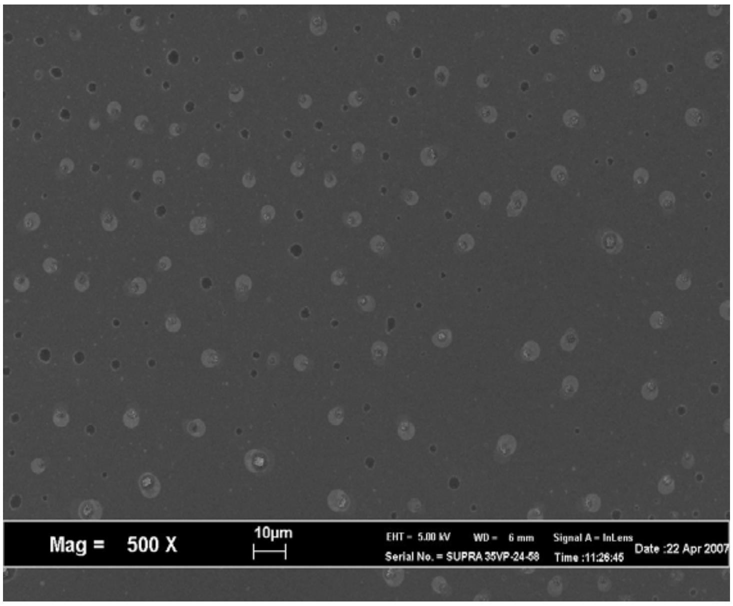

Figure 1: FESEM image of nickel-coated Si substrate.

Figure 3 shows the FESEM image of silicon nanowhisker and EDX analysis on the nanowhisker tip. Meanwhile, Figure 4 shows TEM image of nanowhisker. It was found that both images (FESEM and TEM) show nanosphere at the end of nanowhisker (Figures 3(a) and 4). From EDX analysis obtained the elemental composition of the nanosphere which is 89.05 at% Si, 7.18 at% O and 3.78 at% Ni. This result confirms that the tip is nickel catalyst. Therefore, growth mechanism of this silicon nanostructure is similar to a vapour–liquid–solid (VLS) process. According to this mechanism, the anisotropic crystal growth is promoted by the presence of the liquid alloy/solid interface. This mechanism has been widely accepted and applied for understanding the growth of various one dimensional nanostructures including those of silicon and germanium among others [9]. The VLS mechanism can be divided into three main stages: (a) nucleation, (b) precipitation, and (c) deposition.

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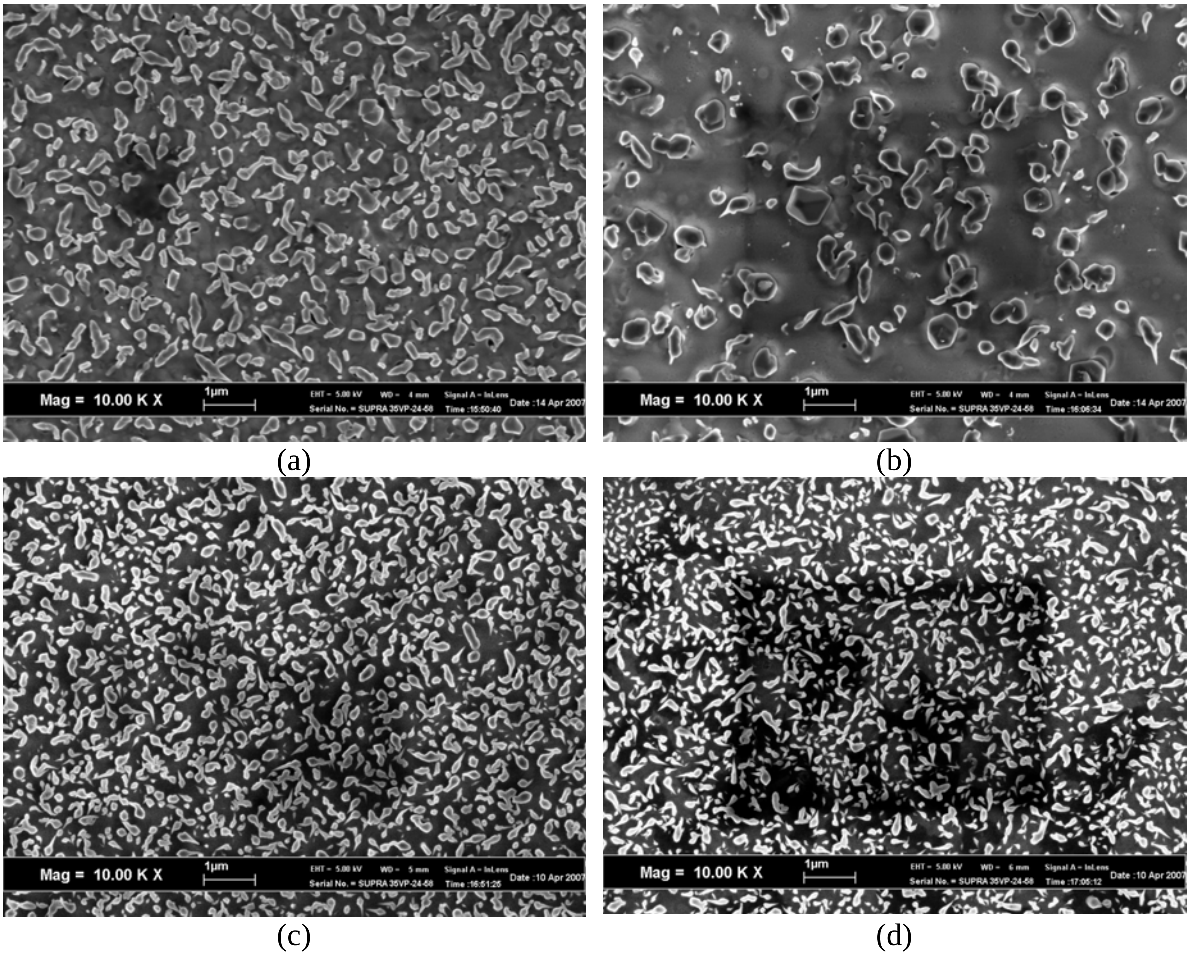

Figure 2: FESEM images of Si nanostructures obtained at substrate location (a) 3 cm, (b) 6 cm, (c) 9 cm, and (d) 12 cm away from source material.

In the nucleation stage, nanosized metallic particles are formed on a substrate. These particles can either be formed by laser ablation or by annealing a very thin metallic film above the eutectic temperature in order to break it into discrete islands. The diameter of the islands thus obtained is typically around 10-20 nm [5]. Then the source material carrier gas is introduced into a chamber maintained above the eutectic temperature. The background pressure is used to control the catalyst size, and the temperature of the tube has to be adjusted in order to maintain the catalyst in the liquid state. The carrier gas reacts in the chamber to form liquid eutectic particles. Then the silicon diffuses through the catalyst droplets. When the eutectic alloy becomes saturated, silicon precipitates at the liquid-solid interface; this is the precipitation. This site is important because it will be a preferred site for further deposition of silicon. The sticking coefficient is higher on liquid than solid surfaces so consequently the crystal growth occurs only where the liquid metallic catalyst is present. In order to grow one dimensional nanostructure array,

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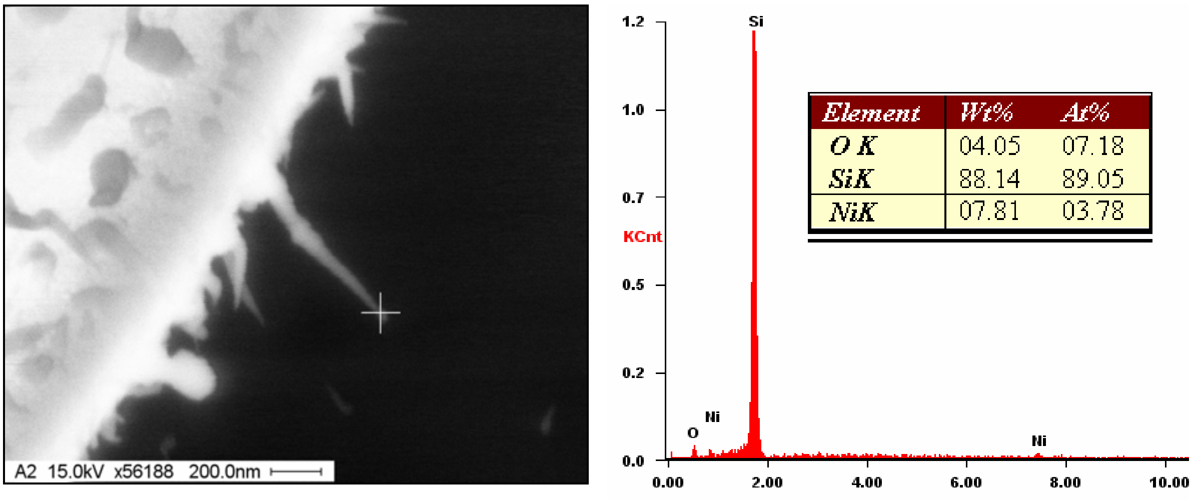
it is important to control the position of the catalyst nanodroplets. Anisotropic growth goes on while the gas flow is maintained; this step is the elongation or the growth itself. At the end of the process, silicon nanowires of high purity are obtained except at one tip, which contains the solidified metallic catalyst. Moreover, a thin layer of native oxide often covers the whole structure. This is mainly due to air ambient native oxidation or remnants of oxygen in the tube.



(a) (b)

Figure 3: (a) FESEM image shows one dimensional nanostructure with sphere at the tip, (b) EDX analysis recorded elemental composition of the tip: 89.05 at% Si, 7.18 at% O and 3.78 at% Ni.

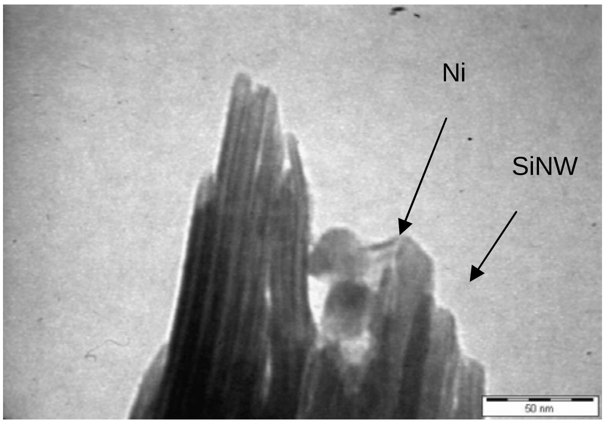


Figure 4: TEM image shows silicon nanowhisker with nanosphere at the tip.

CONCLUSION

The obtained nanostructure products are needle-like silicon nanostructures with spherical shape at the tip. EDX analysis results confirm that the tip is containing nickel element.

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Therefore, the growth mechanism of needle-like silicon nanostructures is similar to a gas phase reaction involving the vapour–liquid–solid (VLS) process.

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REFERENCES

[1] S.-M. Koo, M.D. Edelstein, Q. Li, C.A. Richter, E.M. Vogel, (2005); Nanotechnology, **16**, 1482–1485,
[2] D.W. Kwak, H.Y. Cho, W.C. Yang, (2007); *Physica E*, **37,** 153-157.
[3] A.V. Elder, R.P. Fa, D. Santos, E.F. Silva Jr., B. Henri, (2006); *Applied Surface Science*, **252**, 5572-5574.
[4] W.M. Zhou, F. Fang, Z.Y. Hou, L.J. Yan, Y.F. Zhang, (2006); *IEEE Electron Device Letters*, **27**, 463-465.
[5] C. Guazhong, (2004), *Nanostructures & Nanomaterials; Synthesis, Properties & Applications*, 1st Edition, Imperial College Press, London.
[6] R.S. Wagner and W.C. Ellis, (1964); *Applied Physics Letters*, **4**, 89-90.
[7] P. Nash, (1992); *Phase Diagrams of Binary Nickel Alloy*, Monograph Series on Alloy Ahase Diagram, 6, ASM International, The Material Information Society USA,.
[8] S.D. Hutagalung, K.A. Yacoob, A.F.A. Aziz, (2007); *Applied Surface Science*, **254**, 633-637.
[9] C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, (2003), *Solid State Chemistry*, **31**, 5-147.

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